Photoirradiation Effect on Polymer Light-Emitting Device Based on Poly(3 -dodecylthiophene)

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Photoirradiation effects on a polymer light-emitting device (PLED) from poly(3 -dodecylthiophene) (PAT12) with an ITO/polymer/semitransparent-Al structure have been studied. The effects found in the device from PAT12differ from those found in a device from a poly(p-phenylene vinylene) derivative: the external quantum efficiency of emission from the device as well as the emission intensity at a constant voltage decreases upon photoirradiation. Moreover, while the emission from a PLED based on PAT12diminished upon a photoirradiation in air for several minutes, no notable indication of photooxidation is found in a PAT12film that suffered such a photoirradiation. These suggest that the quenching of the luminescent species by photooxidized defects, rather than the reduced charge transport ability of the polymer, plays a dominant role to diminish the emission.

KEYWORDS:light-emitting device, conducting polymer, poly(3 -alkylthiophene), electroluminescence, photooxidation, quantum efficiency

ポリ(３-ドデシルチオフェン)を用いた高分子発光素子に対する光照射効果

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ポリ(3 -ドデシルチオフェン)(PAT12)を用いたITO/高分子/半透明Al構造の高分子発光素子に対する光照射効果を調べた。PAT12を用いた場合、ポリ(p-フェニレンビニレン)誘導体を用いた素子との相違が見られた：一定電圧における発光強度だけではなく、発光の量子効率までもが光照射によって減少した。さらに、数分間の光照射によって発光は検出されなくなる一方で、光吸収スペクトルの減少は極めて僅かであった。以上の結果は主鎖の切断によるキャリア輸送の阻害ではなく、光酸化欠陥による発光種の消光が劣化の主要因であることを示唆する。

1.Introduction

Polymer light-emitting device (PLED) is one of the most promising candidates for the element in flat-panel displays in the near future, because the easiness of the fabrication of a large polymer thin-film through wet-process helps the production of devices.[1,2] However , PLED is behind the competitors based on inorganic materials in the lifetime and reliability at this stage, and this situation have been stimulating the study on the degradation of PLED.

One of the most important factors to understand the degradation of PLED may be the photooxidation of polymers used in the emission layer. For instance, it is well known that photoluminescence quenching sites such as carbonyl (C=O) groups are formed in the poly(p-phenylene vinylene)-type polymers upon photooxidation.[3,4]

However, in contrast to our deep understanding about the photophysics and photochemistry taking place in the polymers upon photooxidation, what are happening in a PLED upon photooxidation are less known. Since the electroluminescence in a polymer involves not only the photophysics but also the carrier injection/transport phenomena , it is critically important to study the change of the device characteristics upon photooxidation.

Recently, we have carried out some studies on the photooxidation of PLED using the devices having a semitransparent cathode , which enables the photooxidation of the emissive layer after completion of the device fabrication.[5 - 8] In a PLED based on a PPV derivative (MDOPPV), we have found that while the emission intensity at a constant voltage reduces upon photooxidation, the external quantum efficiency of emission does not change.[8]

Poly(3 -alkylthiophene) (PAT) is one of the most widely used polymers in the study of PLED,[9] and the optical patterning of PLEDs from PAT is already reported.[5,7] In this paper , we report the photooxidation effect on the characteristics of a PLED based on poly(3 -dodecylthiophene) (PAT12).

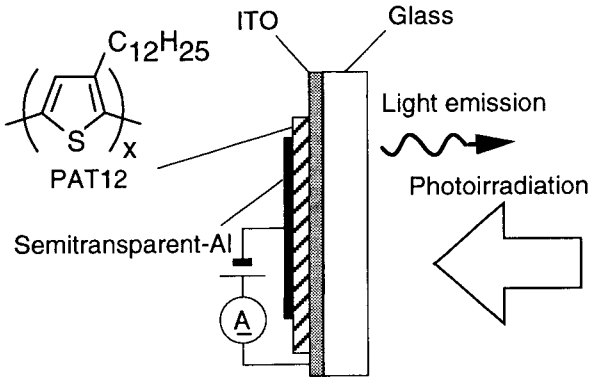

Fig.1 Schematic structure of the PLED used in this study. The molecular structure of poly(3 -dodecylthiophene) (PAT12) is also shown.

2.Experimental

Figure 1 shows the schematic structure of PLED used in this study as well as the molecular structure of PAT12 . The 3 -dodecylthiophene monomer was polymerized with FeCl 3 and was carefully washed according to the literature.[10] Obviously , the PAT12used here has a regiorandom conformation.

The devices were fabricated as follows: a film of PAT12was spin-coated on an indium-tin-oxide (ITO) film coated on a glass substrate from a chloroform solution. The thickness of the PAT12film was of the order of100nm. Then, a semitransparent Al film was vacuum deposited on the polymer surface as a cathode. The Al film was simultaneously deposited on a separate glass plate and the optical transmittance (%T) of it measured at500nm was used as an index of the thickness of the Al cathode. The results shown here were obtained from the devices with %T=24%. Photooxidation was carried out in a slide projector with an150W-incandescent lamp equipped with a thermal-cut filter.

The devices were operated in a dry-box filled with nitrogen at room temperature and the emission intensity-current-voltage characteristics were collected using a PC-controlled measurement system . The emission intensity was measures with a Hamamatsu S1337BQ Si-photodiode attached to the emission face of a device.

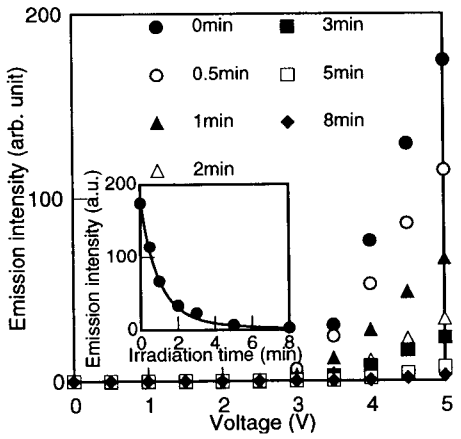

Fig.2 Emission intensity-voltage characteristics of the PLED at various photoirradiation periods. Inset shows the dependence of the emission intensity at 5 V on photoirradiation time.

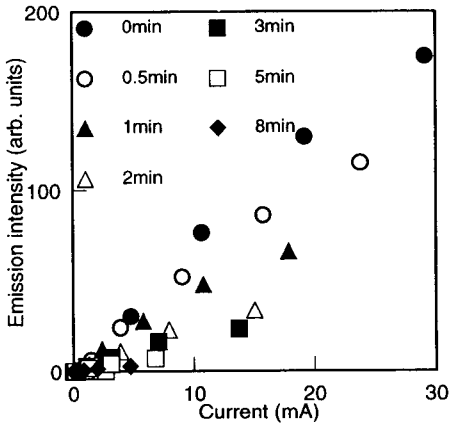

Fig.3 Emission intensity-current characteristics of the PLED at various photoirradiation periods.

Optical absorption spectra were taken with a Hitachi S3140spectrophotometer, and a Riken-Keiki AC- 1 was used for the atmospheric UV photoemission spectroscopy. For these measurements, a naked PAT12film with the same thickness to the PLED was spin-coated on a glass plate and was used.

3.Results and discussion

Figure 2 shows the emission intensity-voltage characteristics of the PLED at various photoirradiation periods. The device before photoirradiation has an onset voltage of emission at 3 V, which does not change upon irradiation. However, the emission intensity of the device at a constant voltage rapidly decreased upon photoirradiation, indicating that although the thickness of Al cathode of the device is slightly thicker than those used in our previous works, the rate of photooxidation is almost the same. As shown in the inset of the figure, the emission smoothly diminished.

The emission intensity-current characteristics of the PLED at various photoirradiation periods are indicated in Fig. 3. In most cases, the emission intensity is proportional to current. It is clearly shown that the slope decreased upon photooxidation, indicating that the external quantum efficiency of the device decreased.

The reduced external quantum efficiency of emission upon photooxidation shown in Fig. 3suggests the formation of defects, which quench the luminescent species such as excitons and exciton-polarons. It is reported that the photooxidation of PAT also results in formation of carbonyl group in the main chain, which may quench the luminescent species. However, unfortunately, the change in photoluminescence spectral change in PAT12due to photooxidation cannot be known because of poor sensitivity of our photoluminescence measurement apparatus.

It can be seen from Figs. 2 and 3, the current at a constant voltage significantly reduced by photooxidation, indicating that the charge injection/transport nature of PAT12is affected. It is expected that this comes from the scission of main

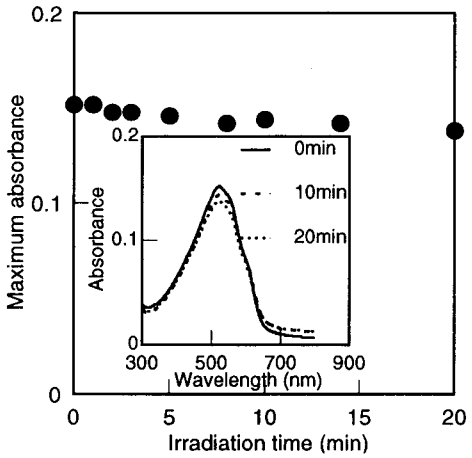

Fig.4 Dependence of the maximum absorbance of the PAT12film on photoirradiation time. Inset shows the absorption spectrum at selected irradiation periods.

chain of PAT12due to photooxidation. However, PAT12itself was found to be relatively robust against the photooxidation. That is, as shown in Fig. 4, only a small change could be observed in the optical absorption spectrum of the PAT12film even after the photoirradiation for20min.

The results mentioned are quite different from the case of the PLED based on MDOPPV [8] as follows:

(i) While the external quantum efficiency of emission in the MDOPPV-device does not change upon photooxidation, that of the PAT12device changes.

(ii) The temporal change of emission intensity at a constant voltage during photoirradiation is different. Namely, while the emission intensity from the MDOPPV-device shows an abrupt change at a certain photooxidation degree, that from the PAT12-device changes smoothly.

(iii)While a significant bleaching of the absorption peak corresponding to _-_* transition is found in the MDOPPV film upon irradiation for several minutes, the PAT12film shows little change.

The reduced quantum efficiency due to photoirradiation indicates that the quenching of the electrically generated luminescent species by photooxidized defects, rather than the reduced charge transport ability of the polymer, plays a dominant role to reduce the emission intensity. The smooth fall in emission intensity due to photooxidation supports this interpretation, because if the reduction of charge transport ability plays a dominant role, an abrupt change corresponding to the formation of a percolation path[12] may be observed. The optical absorption spectra suggest that the photooxidation of PAT12is limited around the polymer/Al interfacial region. In a PLED with an ITO/PAT12/Al structure, the emission zone is expected to localize near the PAT12/Al interface because of the hole-transporting nature of PAT12 . Therefore , the formation of high-density quenching defects at the polymer/Al interface as well as the reduction of electron injection can explain the observations.

It is known that the atmospheric UV photoemission spectroscopy is highly sensitive to the modification of surface. Therefore, the change in the photoemission spectrum of the polymer film during photoirradiation was also measured as indicated in Fig. 5 . Although a slight decrease in photoemission yield due to photooxidation can be found, it is doubtful that this change plays a dominant role in the drastic change in device characteristics. It may be possible that the photochemical modification not of the PAT12film itself but of the PAT12/Al interface is a key for the modification of PLED.

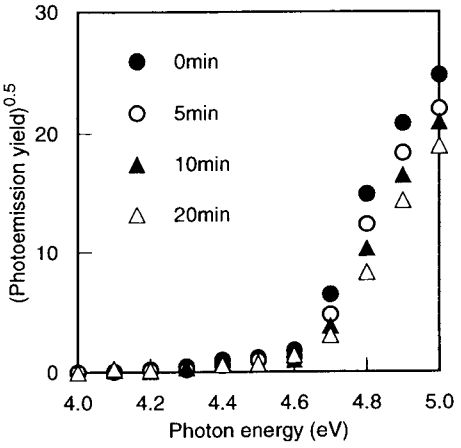

Fig.5 Atmospheric UV photoemission spectrum of the PAT12film at various irradiation periods.

To get deeper understanding , high-energy photoemission spectroscopic studies to analyze modifications of chemical bonds between polymer and cathode through photooxidation should be carried out.

4.Conclusion

Photooxidation effects on a polymer light-emitting device (PLED) from poly(3 -dodecylthiophene) (PAT12) with an ITO/polymer/semitransparent-Al structure were studied . The effects found in the device from PAT12differ from those found in a device from a poly({p-phenylene vinylene) derivative: the emission intensity at a constant voltage as well as the external quantum efficiency of emission from the device decreased upon photoirradiation. Moreover, while the emission from a PLED based on PAT12diminished upon a photoirradiation in air for several minutes, no

notable indication of photooxidation is found in a PAT12film that suffered such a photoirradiation. These suggest that the quenching of the luminescent species by photooxidized defects, rather than the reduced charge transport ability of the polymer, plays a dominant role to diminish the emission.

REFERENCES

[1] R. H. Friend, R. W. Gymer, A. B. Holmes, J. H. Burroughes, R. N. Marks, C. Taliani, D. D. C. Bradley, D. A. Dos Santos, J. L. Br_das, M. L_gdlund and W. R. Salaneck, Nature397(1999)121.

[2] J. Kalinowskii: J. Phys. D: Appl. Phys. 32(1999) R179.

[3] M. Yan, L. J. Rothberg, F. Papadimitrakopoulos, M. E. Galvin and T. M. Miller: Phys. Rev. Lett. 73(1994)744.

[4] L. J. Rothberg, M. Yan, E. W. Kwock, T. M. Miller, M. E. Galvin, S. Son and F. Papadimitrakopoulos, IEEE Trans. Electron Devices44(1997)1258.

[5] K. Tada, M. Onoda and H. Nakayama: Jpn. J. Appl. Phys. 37(1998), L1181.

[6] K. Tada and M. Onoda: J. Appl. Phys. 86(1999)3134.

[7] K. Tada and M. Onoda: Thin Solid Films363(2000)195.

[8] K. Tada and M. Onoda: Appl. Phys. Lett. 77(2000)2539.

[9] Y. Ohmori, M. Uchida, K. Muro and K. Yoshino: Jpn. J. Appl. Phys. 30(1991) L1938.

[10] R. Sugimoto, S. Takeda, H. B. Gu and K. Yoshino: Chem. Express 1 (1986)870.

[11] T. Kawai, T. Kuwabara and K. Yoshino: Jpn. J. Appl. Phys. 31(1992) L49.

[12] R. Zallen: The Physics of Amorphous Solids (John Wiley & Sons, New York, 1983), Chap. 4, p. 188.

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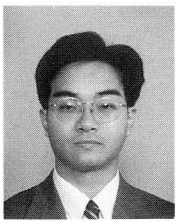

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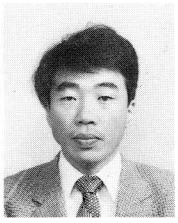

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